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CONTROL OF PHOTOSENSITIZED ELECTRON TRANSFER REACTIONS IN ORGANIZED INTERFACIAL SYSTEMS: VESICLES, WATER-IN-OIL MICROEMULSIONS AND COLLOIDAL SiO_2 PARTICLES

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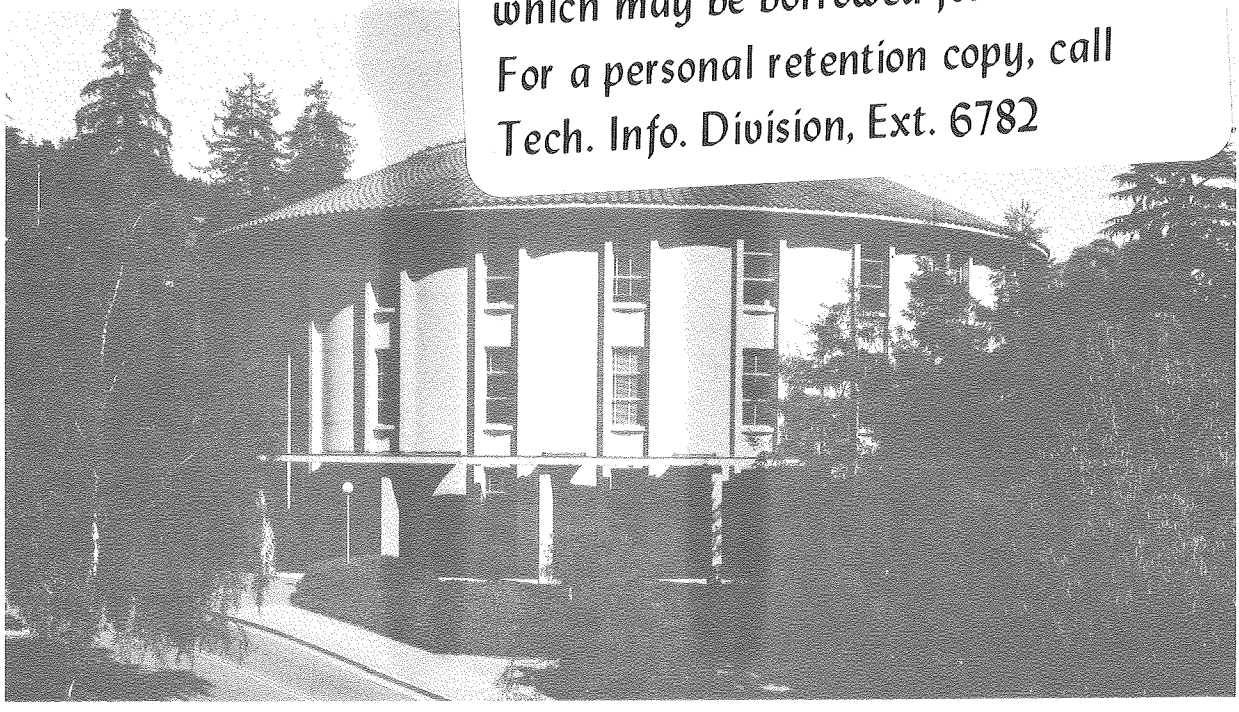

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CONTROL OF PHOTOSENSITIZED ELECTRON TRANSFER REACTIONS IN ORGANIZED INTERFACIAL SYSTEMS: VESICLES, WATER-IN-OIL MICROEMULSIONS AND COLLOIDAL SiO_2 PARTICLES.

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Abstract

The separation of photoproducts formed in photosensitized electron transfer reactions is essential for efficient energy conversion and storage. The organization of the components involved in the photoinduced process in interfacial systems leads to efficient compartmentalization of the products. Several interfacial systems, e.g., lipid bilayer membranes (vesicles), water-in-oil microemulsions and a solid SiO_2 colloidal interface, have been designed to accomplish this goal.

An electron transfer across a lipid bilayer membrane leading to the separation of the photoproducts at opposite sides of the membrane is facilitated by establishing a transmembrane potential and organizing the cotransport of cations with specific carriers.

In the water-in-oil microemulsion the separation of photoproducts is achieved by means of the hydrophilic-hydrophobic nature of the products. A two compartment model system to accomplish the photodecomposition of water is described. Photosensitized electron transfer reactions analogous to those occurring in the two half-cells are presented. In these systems the phase transfer of one of the photoproducts into the continuous oil phase is essential to stabilize the photoproducts.

The colloidal SiO_2 particles provide a charged interface that interacts with charged photoproducts. By designing a system that results in oppositely charged photoproducts, we can produce a retardation of recombination by the charged interface. The photosensitized reduction of a neutral acceptor, propylviologen sulfonate (PVS^o) by positively charged sensitizers such as $Ru(bipy)_3^{2+}$ and Zn-tetramethylpyridinium porphyrin, Zn-$TMPyP^{4+}$, is des-

cribed. The reactions are substantially enhanced in the SiO_2 colloid as compared to those in the homogeneous phase. The effect of the SiO_2 interface is attributed to a high surface potential that results in the separation of the intermediate photoproducts. The quantum yields of the photosensitized reactions are correlated to the interfacial surface potential and the electrical effects of other charged interfaces such as micelles are compared with those of SiO_2.

The possible utilization of the energy stored in the stabilized photoproducts in further chemical reactions is discussed. Special attention is given to the photodecomposition of water as a reaction route.

Reactions in organized media as a means of modeling natural processes are currently an intensive subject of research (1,2). Of particular interest is the subject of "Artificial Photosynthesis", that is, an attempt to create a synthetic apparatus that mimics the functions of the natural process (3,4). The natural photosynthetic cycle leading to the production of carbohydrates (eq.1) can be separated into two major parts (5): a photochemical part, in which visible light is captured and transformed into chemical energy, and a chemical part in which the stored energy is utilized in a sequence of dark reactions. The process is summarized in the "Z-scheme" (Figure 1). The chloroplast utilizes two photosystems composed of well organized pigment molecules. Photoexcitation of these units induces electron transfer reactions that result in the oxidation of water to oxygen and formation of a reduced intermediate (ferredoxin). The reducing power is then used in a set of dark reactions to form carbohydrates from CO_2.

$$H_2O + CO_2 \xrightarrow{h\nu} [CH_2O] + O_2 \qquad \text{(eq.1)}$$

In this article we will discuss several approaches to the design of organized and controlled photosensitized electron transfer reactions. Special emphasis will be given to the utilization of the stored energy in the photodecomposition of water (eq.2).

$$H_2O \xrightarrow{h\nu} H_2 + 1/2\ O_2 \qquad \text{(eq.2)}$$

A schematic cycle describing the principle of light capture and energy storage via a photosensitized electron transfer process in an artificial device is presented in Figure 2. In this system a synthetic sensitizer, S, substitutes for the natural chlorophyll as the light capturing entity. Excitation of the sensitizer, followed by an electron transfer to electron acceptor, A, results in the oxidized sensitizer and a reduced species, A^-. Oxidation of an electron donor, D, recycles the sensitizer and produces an

oxidized product, D^+. In such a way the light energy is transformed into chemical energy and stored in the reduced and oxidized products. The reduced electron acceptor and oxidized electron donor can then be further used to produce hydrogen and oxygen from water, as one example of long term energy storage. In this way all the active components of the system are recycled and the net result is the conversion of water to a potential fuel (hydrogen). However, a basic limitation of such a system is the thermodynamically favored back-electron transfer reactions of the intermediate photoproducts (eq.3 and 4). By these pathways the energy stored in the photochemical event is degraded and an efficient utilization of the photoproducts is prevented.

$$A^- + S^+ \longrightarrow A + S \qquad \text{(eq.3)}$$
$$A^- + D^+ \longrightarrow A + D \qquad \text{(eq.4)}$$

In the natural process this limitation is solved by an organization of the components in a membrane. The two photosystems function at opposite sides of a membrane and consequently the intermediates are separated and an efficient chemical utilization is feasible.

Thus, mimicking photosynthesis with the goal of decomposing water must involve three cooperative elements: (a) A light capturing entity that is capable of photosensitizing electron transfer reactions; (b) an interfacial barrier that separates the intermediate photoproducts and prevents their recombination; and (c) suitable redox catalysts capable of reducing and oxidizing water.

Many synthetic dyes such as porphyrins, acridine, thionine and flavin dyes have been used in photosensitization of electron transfer reactions. In the past few years several promising organometallic compounds have been prepared as substitutes for the natural labile chlorophyll. These organometallics include a variety of metals, chelated to bipyridine or porphyrin ligands (6). The photophysical properties of these sensitizers and their potential use in artificial photosynthetic devices have been extensively reviewed (7, 8, 9). In particular, sensitizers such as Ru(II)-tris-bipyridine, $Ru(bipy)_3^{2+}$(1), and Zn-porphyrins, such as Zn-meso-tetraphenylporphyrins (2) or water-soluble derivatives (3) and (4) have been widely explored. Different structural modifications such as hydrophobic substituents and charged headgroups have also been introduced. Thus, control of electrostatic interactions and precise location of the sensitizer in hydrophilic or hydrophobic environments can be achieved.

The storage of energy by means of a photosensitized electron transfer cycle as presented in Figure 2 requires a close proximity of the components for efficient quenching of the excited species. However, once the photoproducts are produced, their separation must be assisted and a barrier for their recombination must be introduced. Several interfacial systems such as micelles (10,11), water-in-oil (12) or oil-in-water microemulsions (13) and bilayer

membranes (14,15) (vesicles) provide microenvironments that meet these requirements.

Since these interfaces are usually constructed of charged detergents a diffuse electrical double layer is produced and the interfacial boundary can be characterized by a surface potential. Consequently, electrostatic as well as hydrophilic and hydrophobic interactions of the interfacial system can be designed. In this report we will review our achievements in organizing photosensitized electron transfer reactions in different microenvironments such as bilayer membranes and water-in-oil microemulsions. In addition, a novel solid-liquid interface, provided by colloidal SiO_2 particles in an aqueous medium will be discussed as a means of controlling photosensitized electron transfer reactions.

Photosensitized Electron Transfer Across Bilayer Membranes

With the knowledge that membranes play an important role in the natural process, we initiated a study in which bilayer phospholipid membranes (vesicles) serve as an artificial structure. For this purpose an electron transfer across the bilayer boundary must be accomplished (14). The schematic of our system is presented in Figure 3. In this system an amphiphilic Ru-complex is incorporated into the membrane wall. An electron donor, EDTA, is entrapped in the inner compartment of the vesicle, and heptylviologen (HV^{2+}) as electron acceptor is introduced into the outer phase. Upon illumination an electron transfer process across the vesicle walls is initiated and the reduced acceptor ($HV^{+\cdot}$) is produced. The different steps involved in this overall reaction are presented in Figure 3. The excited sensitizer transfers an electron to HV^{2+} in the primary event. The oxidized sensitizer thus produced oxidizes a Ru^{2+} located at the inner surface of the vesicle and thereby the separation of the intermediate photoproducts is assisted (14). The further oxidation of EDTA regenerates the sensitizer and consequently the separation of the reduced species, $HV^{+\cdot}$, from the oxidized product is achieved. In this system the basic principle of a vectorial electron transfer across a membrane is demonstrated. However, the quantum yield for the reaction is rather low ($\phi = \sim 4 \times 10^{-4}$).

The transmembrane electron transfer was found to be the rate limiting factor for the overall reaction and the origin of the low efficiency. The electron transfer across the membrane must be followed by cotransport of cations in order to keep charge neutrality. Since the membrane has a low permeability to such cations, the photosensitized reaction might be limited by this effect. Indeed, further elaboration of the vesicle system by including cation carriers can improve the photoinduced reaction. For this purpose hydrophobic cation carriers (ionophores) such as valinomycin (specific for K^+) CCCP (specific for H^+) and gramicidin(transport agent of K^+, Na^+ and H^+) have been incorporated into the hydrophobic region of the vesicles (16). The photosensitized electron

transfer reaction in the presence of these carriers is enhanced to a 3-6 fold extent, depending on the ionophore (Figure 4A). These results confirm that the cotransport of cations plays an important role in the photosensitized reactions.

In addition to their function in establishing charge neutralization during the photochemical reactions, cations might, by proper organization, even assist the electron transfer via production of a transmembrane potential. Different concentrations of K^+ in the opposite aqueous phases of the lipid bilayer were used to test for this effect. The specific K^+ carrier, valinomycin, was incorporated into the vesicle walls. Consequently, owing to the concentration difference, a long-lasting transmembrane potential is established. The photosensitized electron transfer reaction appears to be affected by such electric fields (Figure 4B). It can be seen that when the ratio of $K^+_{in}/K^+_{out} > 1$, i.e., interior boundary negative relative to the exterior, the reaction is 2-fold enhanced as compared to the system without any applied field. Conversely, when the vesicles are designed such that $K^+_{in}/K^+_{out} < 1$ and an opposite potential is formed, the quantum yield is decreased and approaches the value obtained in the absence of any valinomycin (16). We can see that the combined effects of cation permeability and a transmembrane potential result in an 11-fold enhancement in the photosensitized reduction of heptylviologen (HV^{2+}). Thus, proper organization of different components in the lipid bilayer interfacial system can enhance electron transfer reactions and assist the separation of photoproducts across the bilayer.

Photosensitized Electron Transfer in Water-in-Oil Microemulsions

A water-in-oil microemulsion is an interfacial system of aqueous droplets in a continuous oil phase. By including water soluble or amphiphilic reagents in this system, the components can be concentrated at will in the different phases of the microemulsion. By selecting an electron donor or electron acceptor that alters its amphiphilic properties upon oxidation or reduction, one of the photoproducts can be extracted into the continuous organic phase and so the separation of the photoproducts in two distinct phases is achieved.

A possible model system is composed of two compartment that include water-in-oil microemulsions represented in Figure 5 as two droplets. In the aqueous phases of the two compartments two different sensitizers, S_1 and S_2 are solubilized. In one compartment, an electron acceptor, A_2, is solubilized in the aqueous phase while the electron donor, D_2, is concentrated at the interface of the microemulsion. In the complementary half-cell the electron donor, D_1, is solubilized in the water droplets and the electron acceptor, A_1, is localized at the interface. The electron donor, D_2, and electron acceptor, A_1, are designed in such a way that oxidized D_2 and reduced A_1 are extracted into the continuous organic phase. The photosensitized reactions initiated in the two

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By means of these interactions a component can be selectively adsorbed to the interface and its recombination with an oppositely charged photoproduct can be retarded.

To achieve such an organization in the system the different components have to be functionalized. Two positively charged sensitizers, $Ru(bipy)_3^{2+}$ (1) or Zn-meso-tetramethylpyridinium porphyrin, $Zn\text{-}TMPyP^{4+}$ (3), that are adsorbed to the SiO_2 interface are used (19). The zwitterionic dipropylsulfonate-4,4'-bipyridinium (5) (propylviologen sulfonate, PVS^o) is used as electron acceptor, and triethanolamine, TEA, is introduced as electron donor. Photosensitized electron transfer in these systems results in a rapid production of the viologen radical, $PVS^{-\cdot}$. The rates of $PVS^{-\cdot}$ formation in the colloidal SiO_2 systems using the different sensitizers are shown in Figure 7, and compared with the analogous reactions in a homogeneous phase. It can be seen that the electron transfer reactions in the SiO_2 colloid are ca. 10-fold enhanced relative to the homogeneous phase and using $Zn\text{-}TMPyP^{4+}$ as sensitizer a high quantum yield ($\phi = 0.35$) is obtained. The enhanced quantum yields in the SiO_2 colloids are ascribed to the control of the electron transfer reaction by means of electrostatic interactions (eq. 5 and 6 and Figure 8). The electron transfer from the excited sensitizer, $Ru(bipy)_3^{2+}$, to the neutral electron acceptor results in two oppositely charged photoproducts. The charged interface interacts with these intermediate photoproducts; the oxidized sensitizer is adsorbed at the interface while the reduced, negatively charged electron acceptor is repelled. Consequently, the electrostatic interactions introduce a barrier to the degradative geminate recombination of the photoproducts. As a result, the further effective utilization of the oxidized product, $Ru(bipy)_3^{3+}$, in oxidizing the electron donor, TEA, is facilitated and high quantum yields are obtained.

$$Zn\text{-}TMPyP^{4+} + PVS^o \underset{k_b}{\overset{h\nu}{\rightleftharpoons}} Zn\text{-}TMPyP^{5+} + PVS^{-\cdot} \quad \text{(eq.5)}$$

$$Ru(bipy)_3^{2+} + PVS^o \underset{k_b}{\overset{h\nu}{\rightleftharpoons}} Ru(bipy)_3^{3+} + PVS^{-\cdot} \quad \text{(eq.6)}$$

The function of the SiO_2 colloid in retarding back-electron transfer reactions has been confirmed by several methods:

(a) The quantum yield in the SiO_2 colloid depends strongly on the ionic strength of the medium. By increasing the ionic strength the interfacial surface potential is decreased. As a result, the electrostatic interactions with the interface are reduced and the quantum yield is decreased.

(b) Substitution of the positive sensitizer with one that is negatively charged yields two photoproducts that are repelled by the interface. Thus, the function of the interface in separating the active intermediates is lost. Indeed, with a negatively charged sensitizer, Zn-meso-tetraphenylporphyrin sulfonate, $Zn\text{-}TPPS^{4-}$ (4),

there is no enhancement of quantum yield in the SiO_2 system (Figure 7B).

(c) The back-electron transfer reaction of the intermediate photoproducts (eq. 5 and 6) has been directly followed in the SiO_2 colloid by means of flash photolysis and compared to the similar process in a homogeneous phase. A significant retardation of back-electron transfer is observed. With Zn-TMPyP^{4+} as sensitizer, the recombination rate constant (eq.5) in the SiO_2 colloid is reduced by a factor of 100 relative to the value in a homogeneous phase. Similarly, with $Ru(bipy)_3^{2+}$ as sensitizer the recombination rate is ca. 90-fold retarded in the SiO_2 colloid.

The extent to which back-electron transfer reactions are retarded in the SiO_2 colloid can be improved by introduction of multinegatively charged electron acceptors such as $Fe(CN)_6^{3-}$ that increase the repulsive interactions with the interface (20). However, with such electron acceptors the primary electron transfer event is expected to be rather inefficient because they cannot approach the interface. In order to keep the balance of efficient quenching of the excited state, together with a substantial retardation of the recombination rate, two coupled electron acceptors can be used. For this purpose, a colloidal SiO_2 system has been designed in which $Ru(bipy)_3^{2+}$ is the sensitizer, PVS^o (5) the primary electron acceptor and triethanolamine, TEA, the electron donor. A secondary electron acceptor, $K_3Fe(CN)_6$, is introduced into the system to provide a sink for the electron (Figure 9). The complete photosensitized electron transfer process results in the reduction of $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$ (Figure 10). It appears that the photosensitized reaction is at least 60-fold enhanced relative to the reaction in a homogeneous phase (20). The sequence of events occurring in this photosensitized electron transfer have been followed by flash photolysis. The reduced primary electron acceptor $PVS^{\cdot}$ is produced by the quenching of the excited sensitizer adsorbed to the SiO_2 interface (eq.6). The reduced species is ejected into the continuous aqueous phase where $Fe(CN)_6^{3-}$ is reduced (eq. 7) in a "dark" reaction. The intermediate photoproducts thus created, $Ru(bipy)_3^{3+}$ and $Fe(CN)_6^{4-}$, tend to back-react (eq.8). In a homogeneous system this process is diffusion controlled ($k_b \approx 10^{10} M^{-1}.sec^{-1}$)(21). However, in the SiO_2 colloid a substantial inhibition of the recombination rate is observed ($k_b = 10^6-10^7\ M^{-1}.sec^{-1}$). These results indicate that the different functions required for an efficient electron transfer process can be achieved by coupling two or more electron acceptors.

$$PVS^{\cdot} + Fe(CN)_6^{3-} \longrightarrow PVS^o + Fe(CN)_6^{4-} \qquad \text{(eq.7)}$$

$$Ru(bipy)_3^{3+} + Fe(CN)_6^{4-} \xrightarrow{k_b} Ru(bipy)_3^{2+} + Fe(CN)_6^{3-} \qquad \text{(eq.8)}$$

Correlation of Quantum Yields with Interfacial Potentials

The function of the SiO_2 colloid in the photosensitized electron transfer originates from selective interactions of the components with the interface. The electrical properties of the interface and the binding characteristics of the positively charged sensitizer, $Ru(bipy)_3^{2+}$, have been examined by means of flow dialysis ($K_{ass.} = 1.1 \times 10^2\ M^{-1}$)(22). The number of binding sites on each SiO_2 particle has been determined to be 65. These ionic sites establish an interfacial surface potential of ca. -170 mV.

The quantum yield for the photosensitized reduction of PVS^o (using $Ru(bipy)_3^{2+}$ as sensitizer) has been correlated with the interfacial surface potential of the SiO_2 colloid (controlled by varying the ionic strength of the medium) (22). The correlation curve (Figure 11) shows that up to an interfacial potential of ca. -40 mV the quantum yield is not affected. Increasing the potential above this apparent threshold value results in a sharp increase in the quantum yield. A similar correlation curve was obtained when $Zn\text{-}TMPyP^{4+}$ was used as sensitizer instead of $Ru(bipy)_3^{2+}$.

The organization of components in the SiO_2 colloids and the electrostatic interactions could, in principle, be designed with other negatively charged interfaces such as micelles. The photosensitized reduction of PVS^o using $Ru(bipy)_3^{2+}$ as sensitizer and triethanolamine, TEA, as electron donor has been investigated in the presence of negatively charged NaLS micelles and compared to the results in the SiO_2 colloid (Figure 7A) (22). The size of the NaLS micelles is similar to that of the SiO_2 particles. The sensitizer, $Ru(bipy)_3^{2+}$, appears to bind firmly to the micellar interface ($K_{ass.} = 3.5 \times 10^3\ M^{-1}$). Yet, the quantum yield for the PVS^- formation is 4-fold less efficient than that observed in the SiO_2 colloid. This result is attributed to the difference in the surface potential of the two interfaces. Flow dialysis measurements (22) indicate that the NaLS micellar interface has a surface potential of only -85 mV, significantly lower than the value determined for the SiO_2 interface (-170 mV). The experimental quantum yields in the NaLS micellar system fit nicely into the correlation curve shown in Figure 11. This indicates that due to the relatively low surface potential of the micelles the electrostatic interactions are not as effective. The comparison of photoinduced reactions in the SiO_2 colloid to that occurring in the NaLS micelles implies that both interfaces are capable of exerting electrostatic interactions. This can be used for organizing the components involved in the photochemical reaction. However, the physical characteristics of the electric field of the different interfaces is rather important in controlling the reaction. In the NaLS micellar system, despite the organization of the components, the surface potential is relatively low and limits the ability to retard back reaction.

Chemical Utilization of the Photoproducts in the Photodecomposition of Water

The different interfacial systems described in this paper represent supramolecular assemblies for the separation and stabilization of photoproducts. These photoproducts generated in the electron transfer reactions are an oxidized sensitizer and a reduced species (acceptor). In all systems that have been described here a sacrifical electron donor (EDTA or TEA) has been used. For any practical configuration, this sacrificial component must be excluded and water itself should be the compound oxidized. The oxidized intermediates, $Ru(bipy)_3^{3+}$ and $Zn\text{-}TMPyP^{5+}$, have the potential for oxidizing water to oxygen ($E_o(Ru(bipy)_3^{3+}/Ru(bipy)_3^{2+}) = 1.26$ volt; E_o ($Zn\text{-}TMPyP^{5+}/Zn\text{-}TMPyP^{4+}$) = 1.2 volt), but since the reaction requires a concerted four-electron process while the photoproducts are single electron oxidants, a mediating charge-storage catalyst is needed. In recent years transition metal oxides and, in particular, RuO_2 and PtO_2, have been reported to act as oxygen evolution catalysts with $Ru(bipy)_3^{3+}$ as oxidant (23,24). In an analogous way, the reduced species produced in the photosensitized reaction should be coupled to hydrogen evolution. Reduced bipyridinium salts (viologen radicals) are capable of reducing water to hydrogen (25, 26). For this reaction colloidal platinum has been found to be an efficient charge-storage catalyst.

A schematic view of one possible complete system is shown in Figure 12. Since the oxidized photoproduct, e.g., $Ru(bipy)_3^{3+}$, is associated with one colloidal particle, its interface should be coated with an oxygen-evolving catalyst. An additional colloidal site is introduced by supporting platinum on a negatively charged polymer. The electrostatic repulsions of the two negatively charged interfaces would prevent agglomeration. By using a polymer with a low enough surface potential the approach of the reduced photoproduct, PVS^{-}, to the hydrogen evolution catalyst would be permitted while its recombination with $Ru(bipy)_3^{3+}$ on the other, more highly charged colloid, would be prevented. In this way, the vectorial character of the electron transfer process could be used for an efficient cleavage of water.

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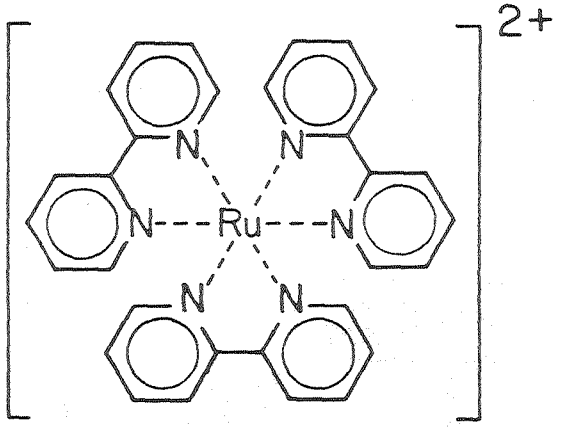

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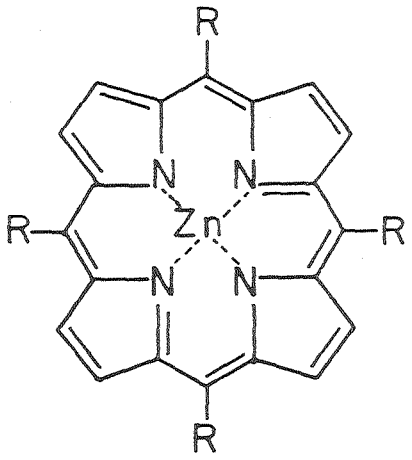
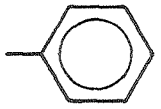
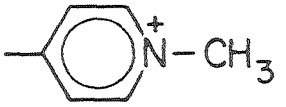
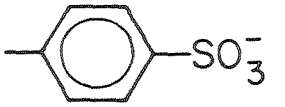
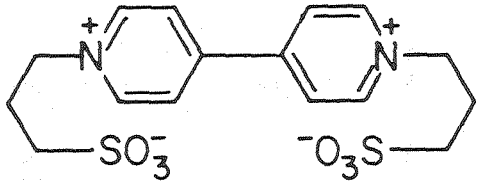


R =  (2)

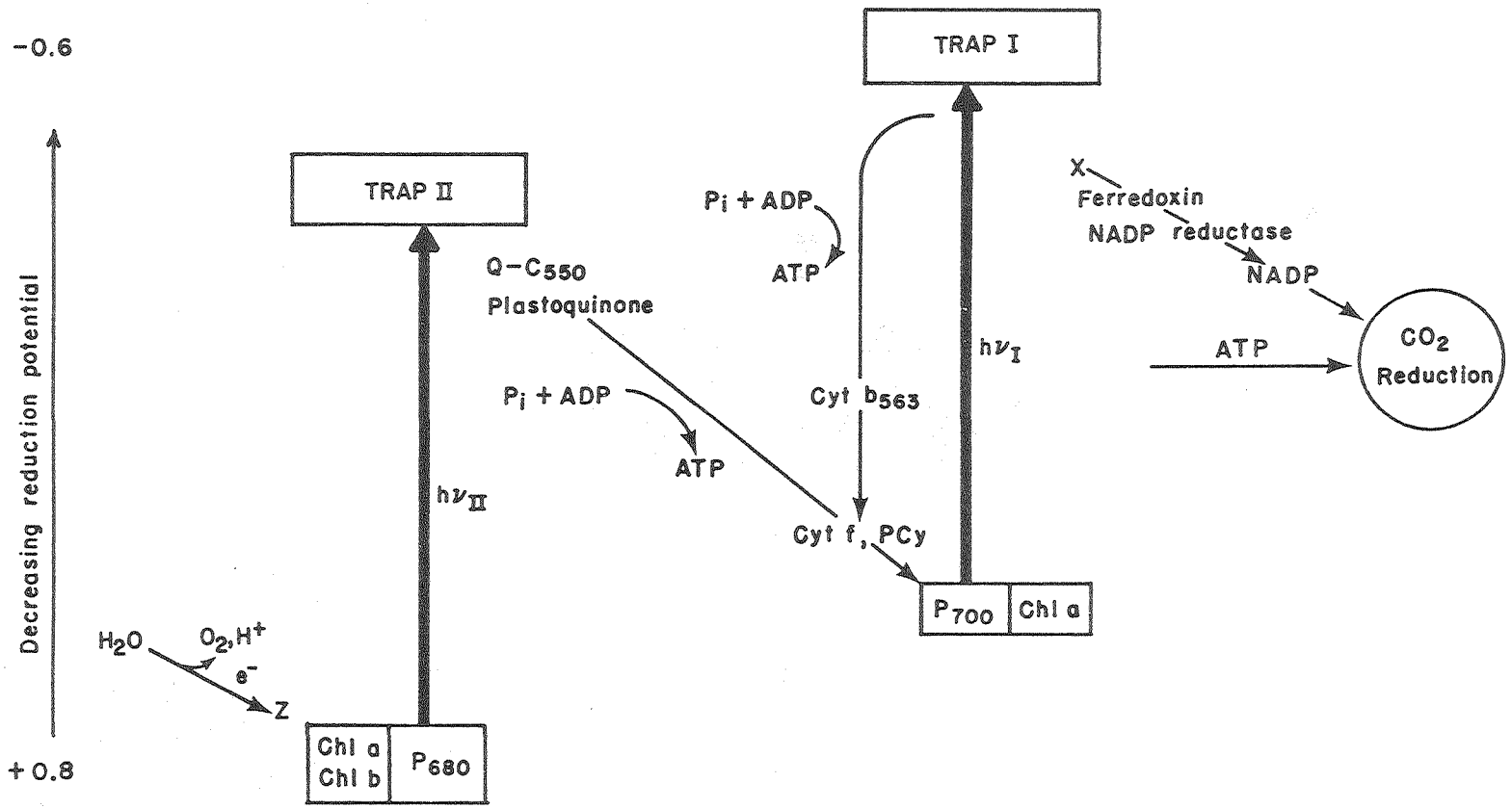
R =  (3)

R =  (4)



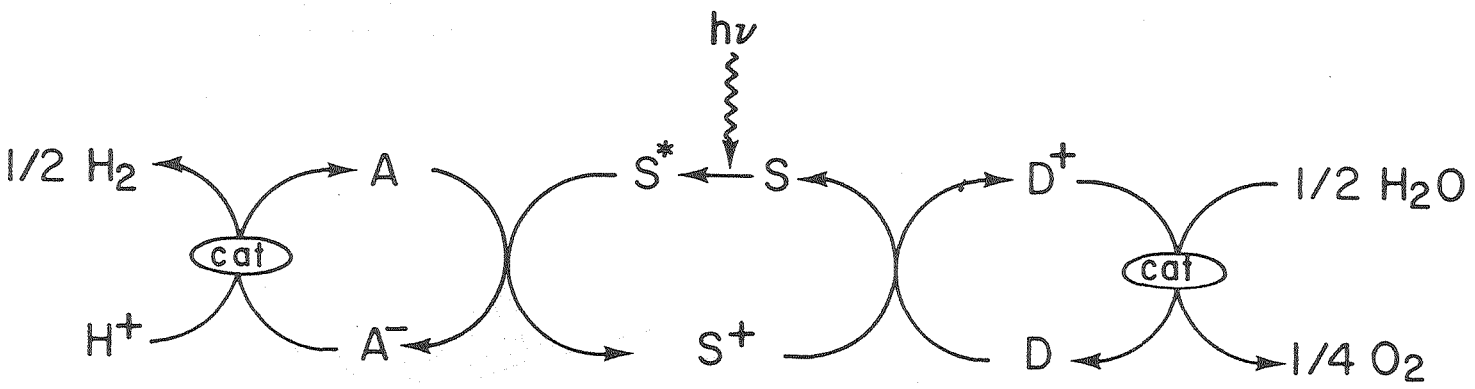
(5)

XBL 814-4530A



XBL7410-5395 B

Figure 1. Electron transfer (Z-scheme) in photosynthesis



Cyclic Photochemical Scheme for
Decomposition of Water

XBL 812-4459

Figure 2. General scheme for water decomposition.
S represents artificial sensitizer which simulates the function of the natural chlorophyll. "Cat" represents catalyst

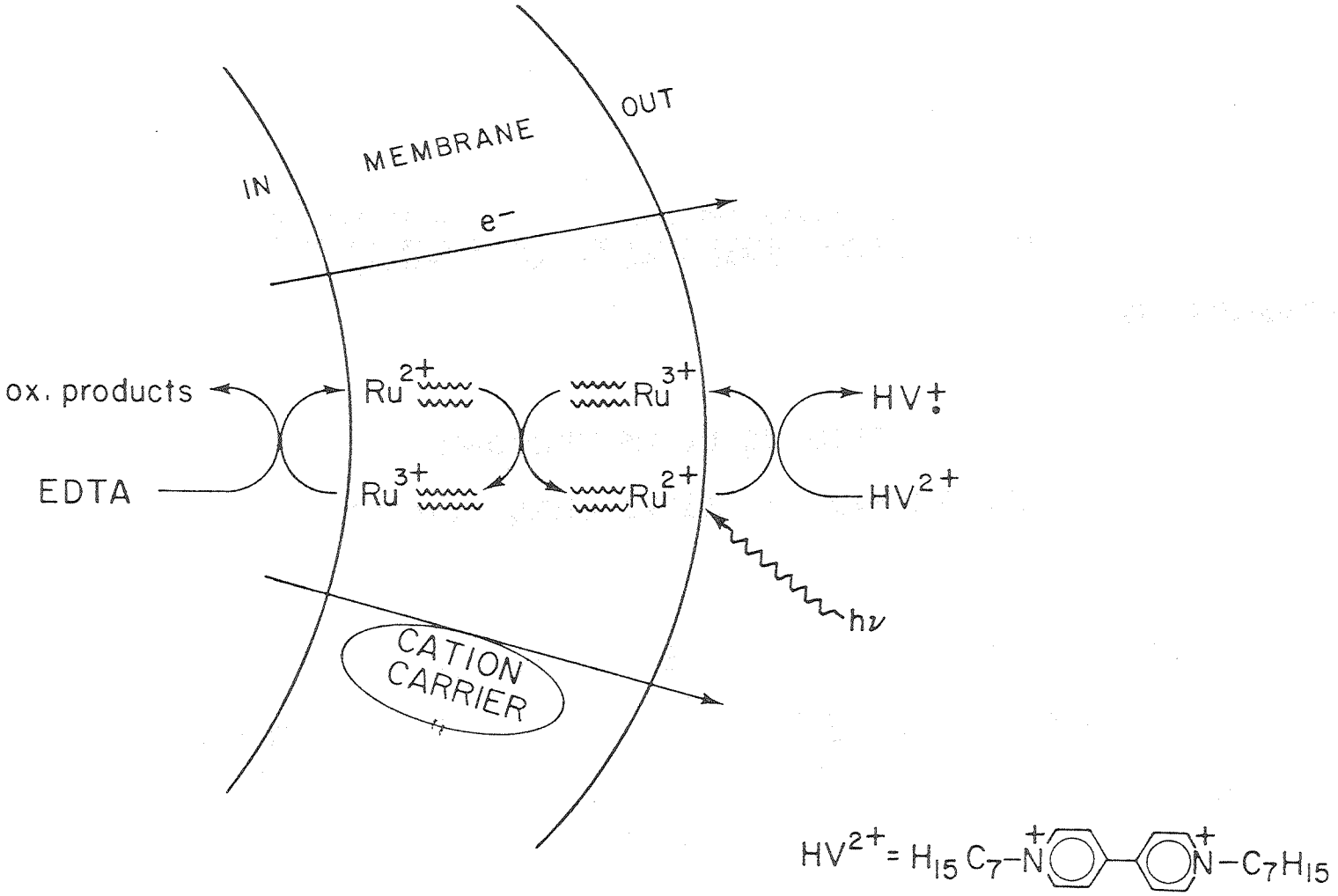


Figure 3. Scheme for photosensitized electron transfer across a lipid vesicle wall.

XBL 814-4541A

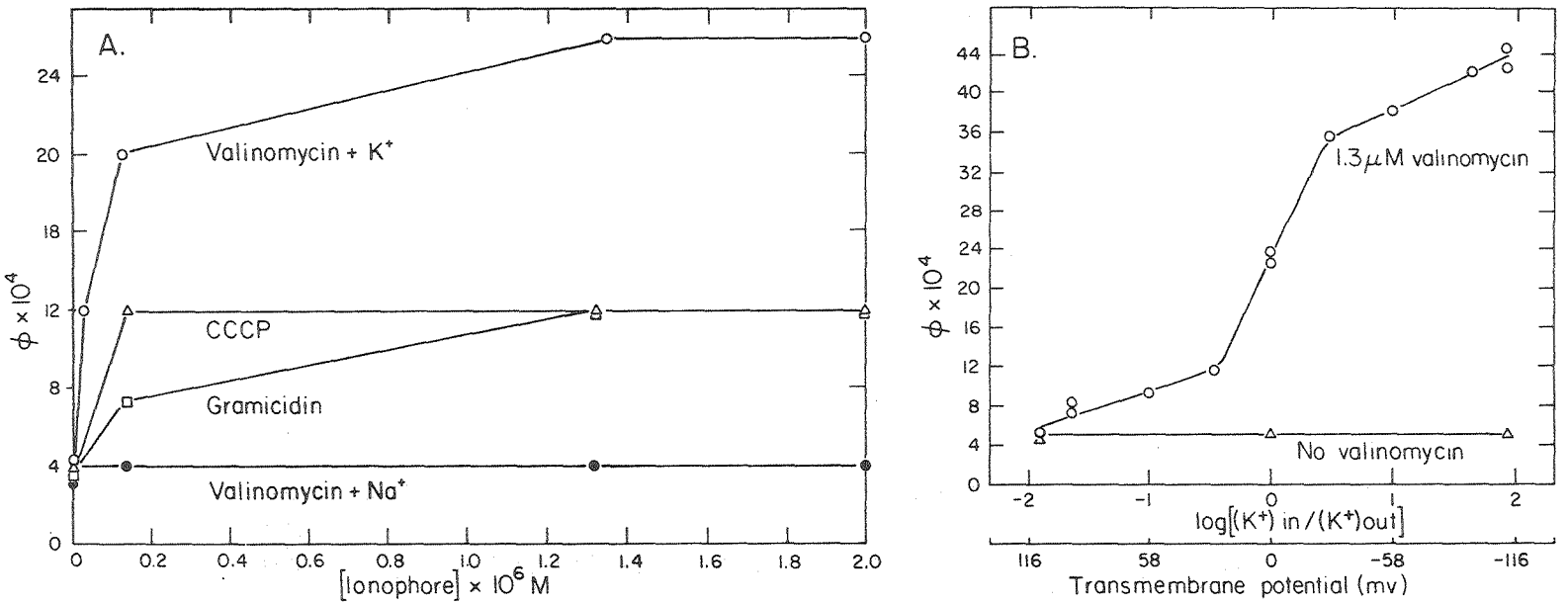


Figure 4. Effect of ionophores (A) and transmembrane potentials (B) on quantum yield of heptulviologen reduction in the vesicle system. $\emptyset$ = quantum yield; CCCP (carbonyl cyanide m-chlorophenylhydrazone), H^+ carrier; valinomycin, K^+ carrier; gramicidin makes membrane permeable for several cations such as H^+, K^+, Na^+

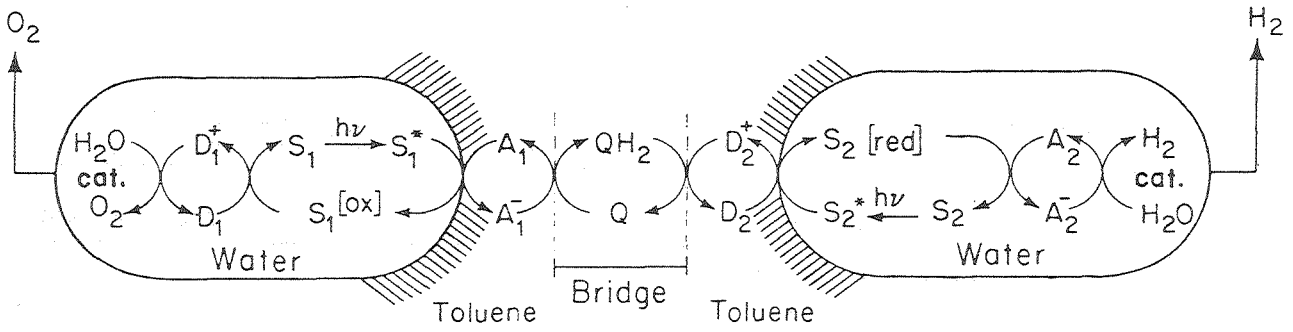


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Figure 5. General scheme for water photodecomposition using two half-cells of water-in-oil microemulsions

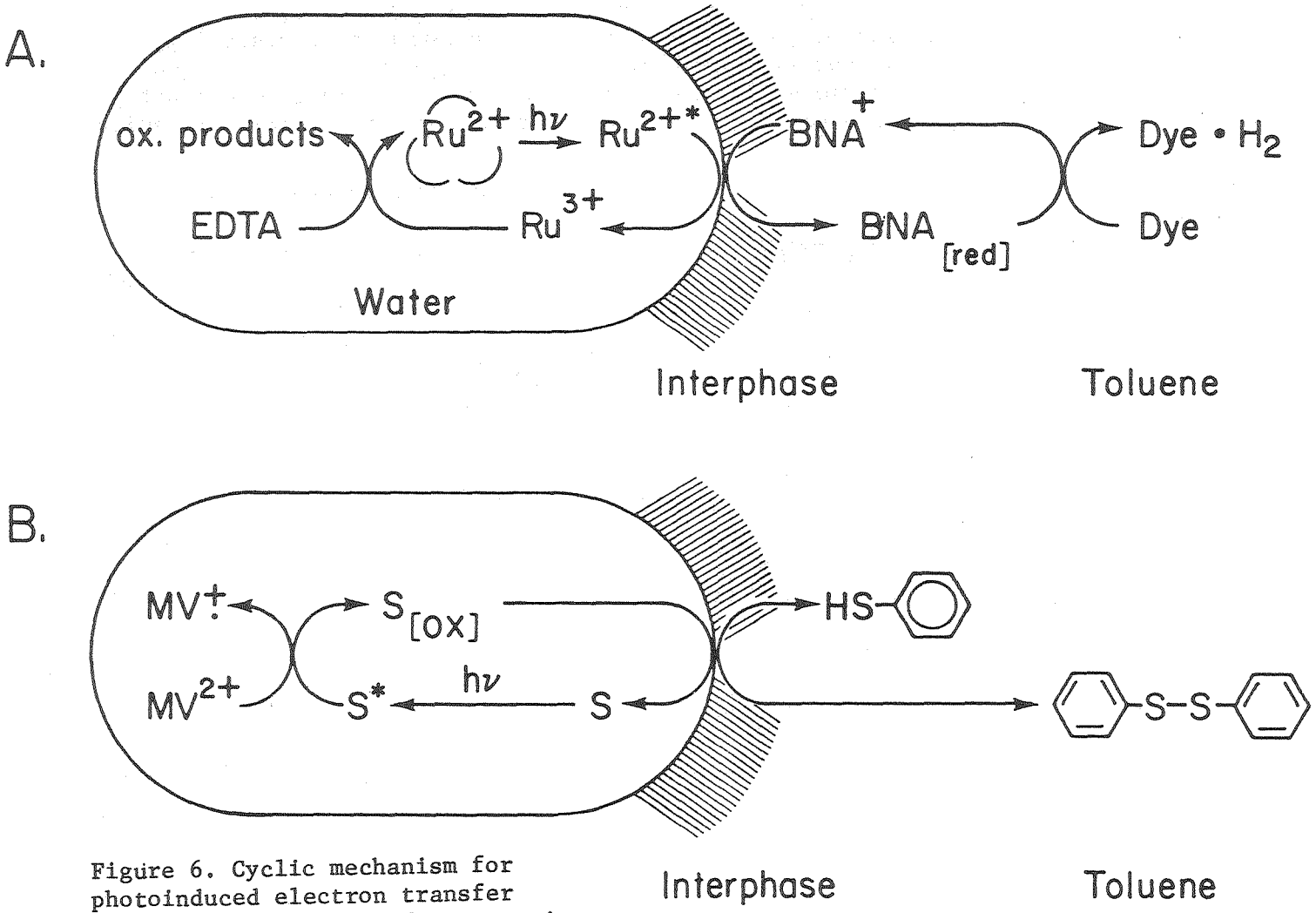


Figure 6. Cyclic mechanism for photoinduced electron transfer across the interface of a water-in-toluene microemulsion. (A) Oxidative half-cell; (b) reductive half-cell

XBL 814-4531

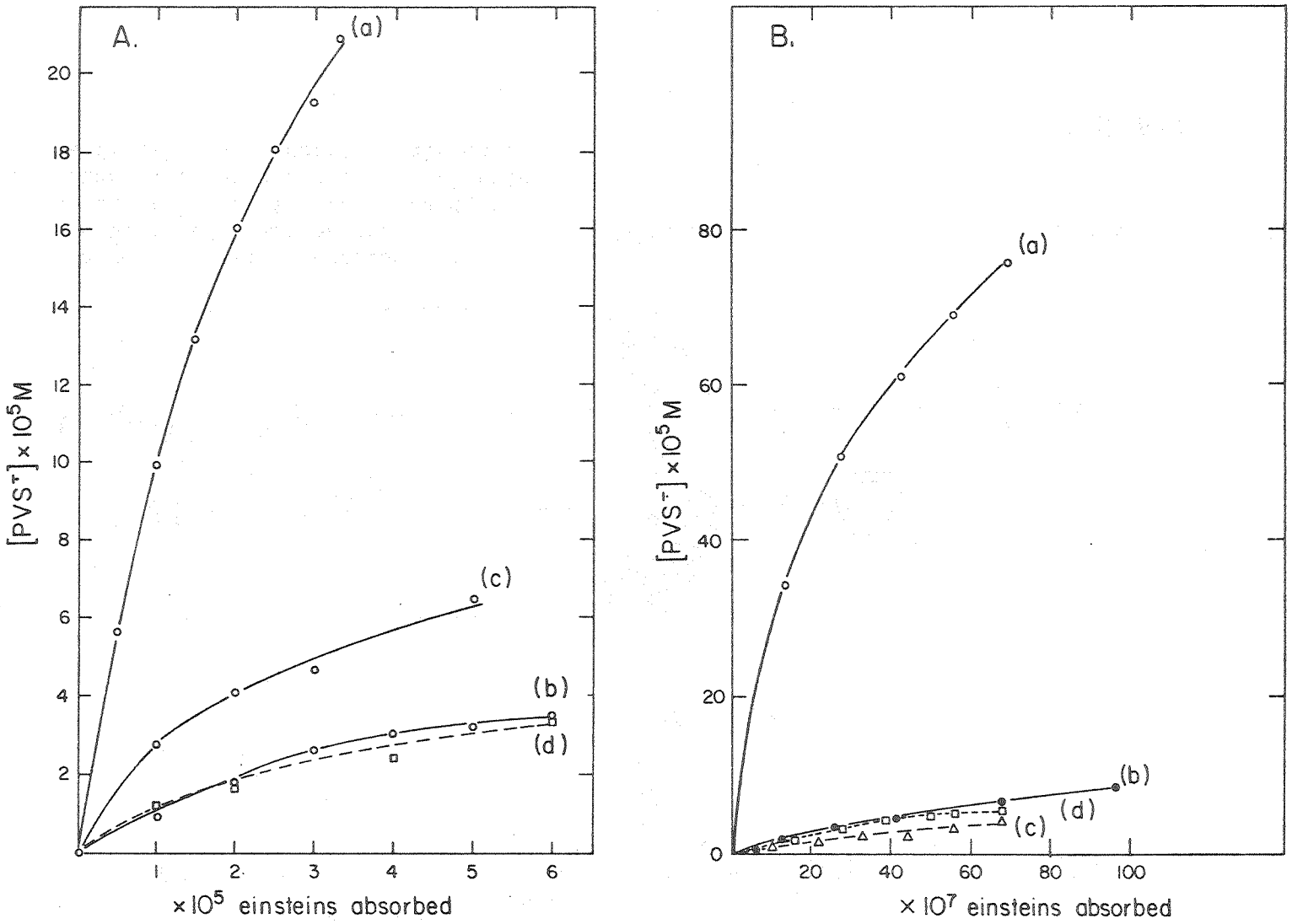
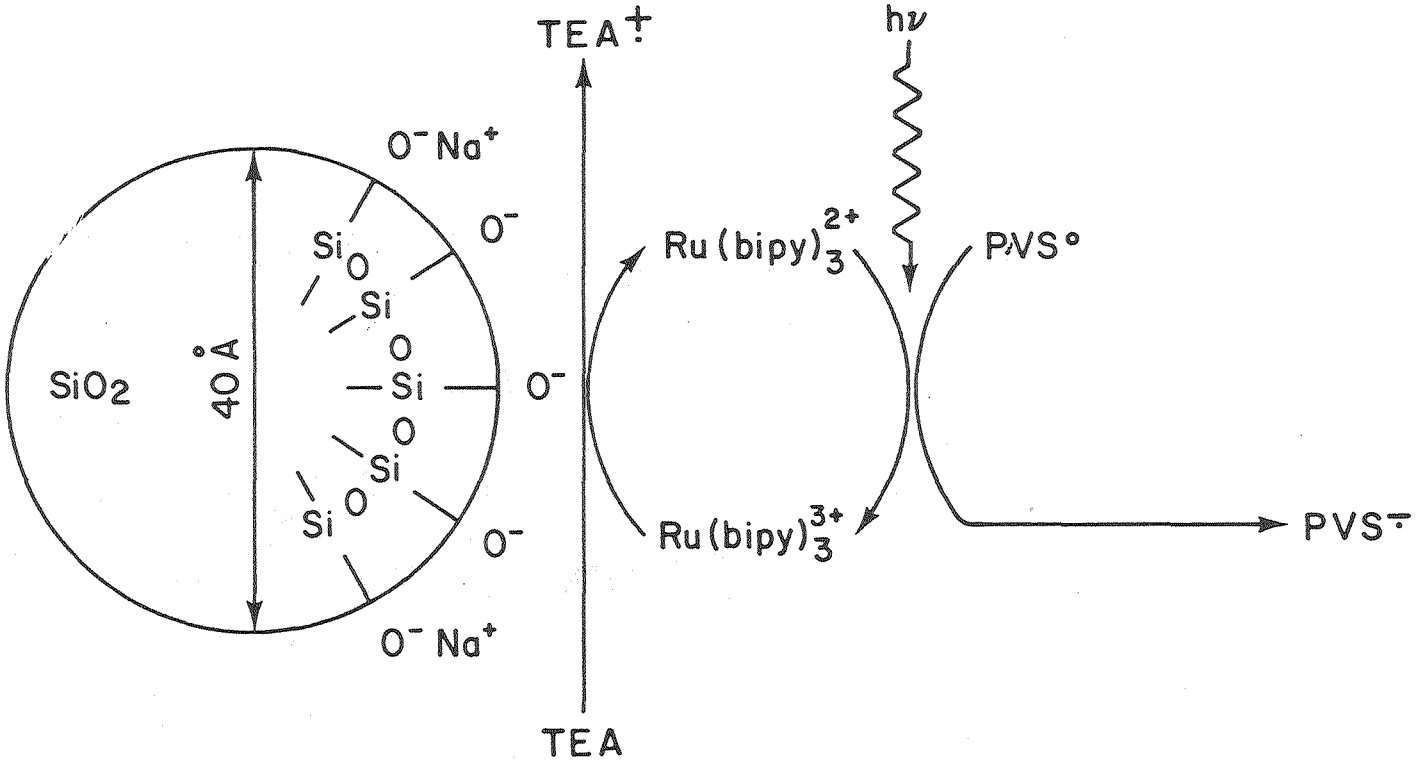


Figure 7. Propylviologen radical, $PVS^{\cdot}$, formation as a function of light adsorbed, monitored by the increase of absorbance at = 602 nm. (= 12500 $M^{-1}cm^{-1}$). (A) $Ru(bipy)_3^{2+}$ as sensitizer; (a) SiO_2 system; (b) homogeneous system; (c) micellar system; (d) NaLS micellar system with 0.1 M NaCl. (B) Zn-$TMPyP^{4+}$ and Zn-$TPPS^{4-}$ as sensitizers; (a) SiO_2 system with Zn-$TMPyP^{4+}$; (b) homogeneous system with Zn$OTMPyP^{4+}$; (c) SiO_2 system with Zn-$TPPS^{4-}$; (d) homogeneous system with Zn$OTPPS^{4-}$.

XBL 814-4529



XBL 811-4426

Figure 8. Schematic function of SiO_2 particles in separating photoproducts

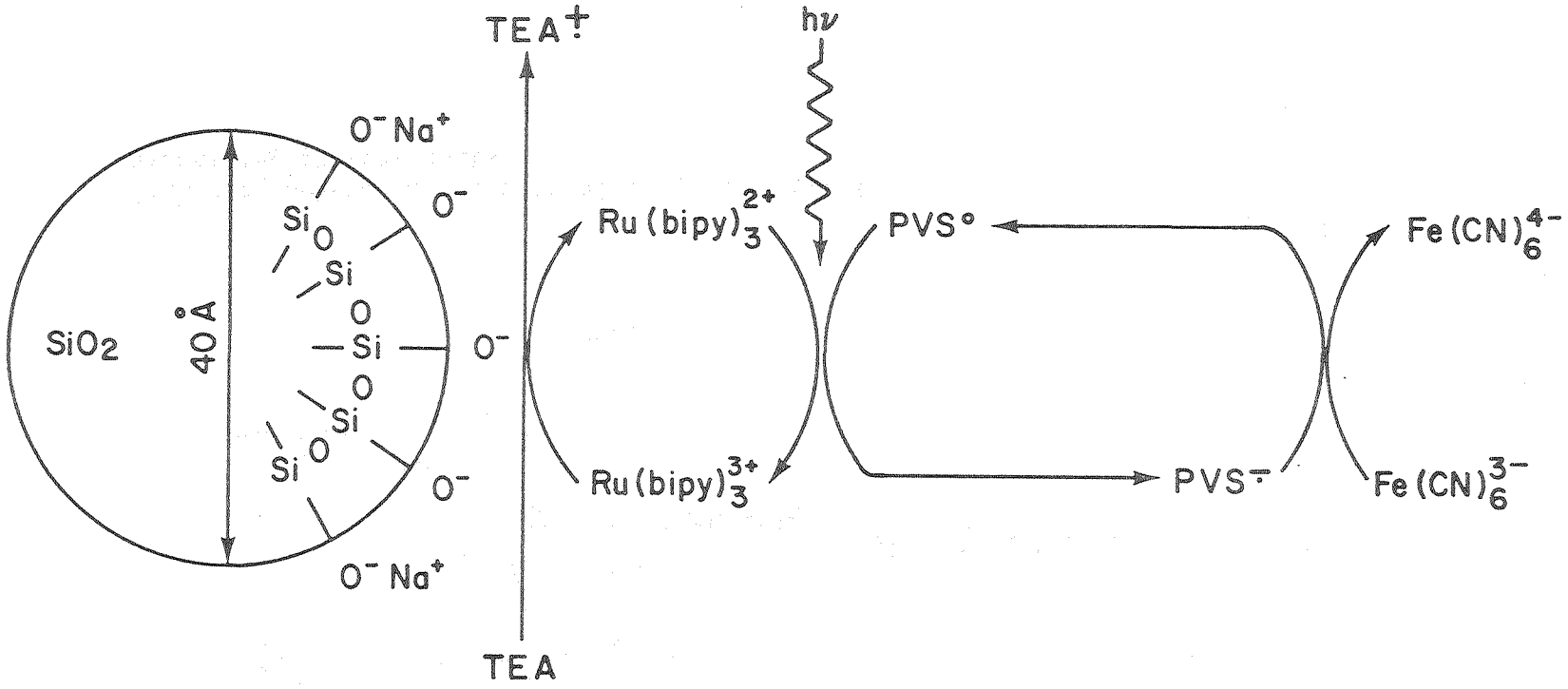
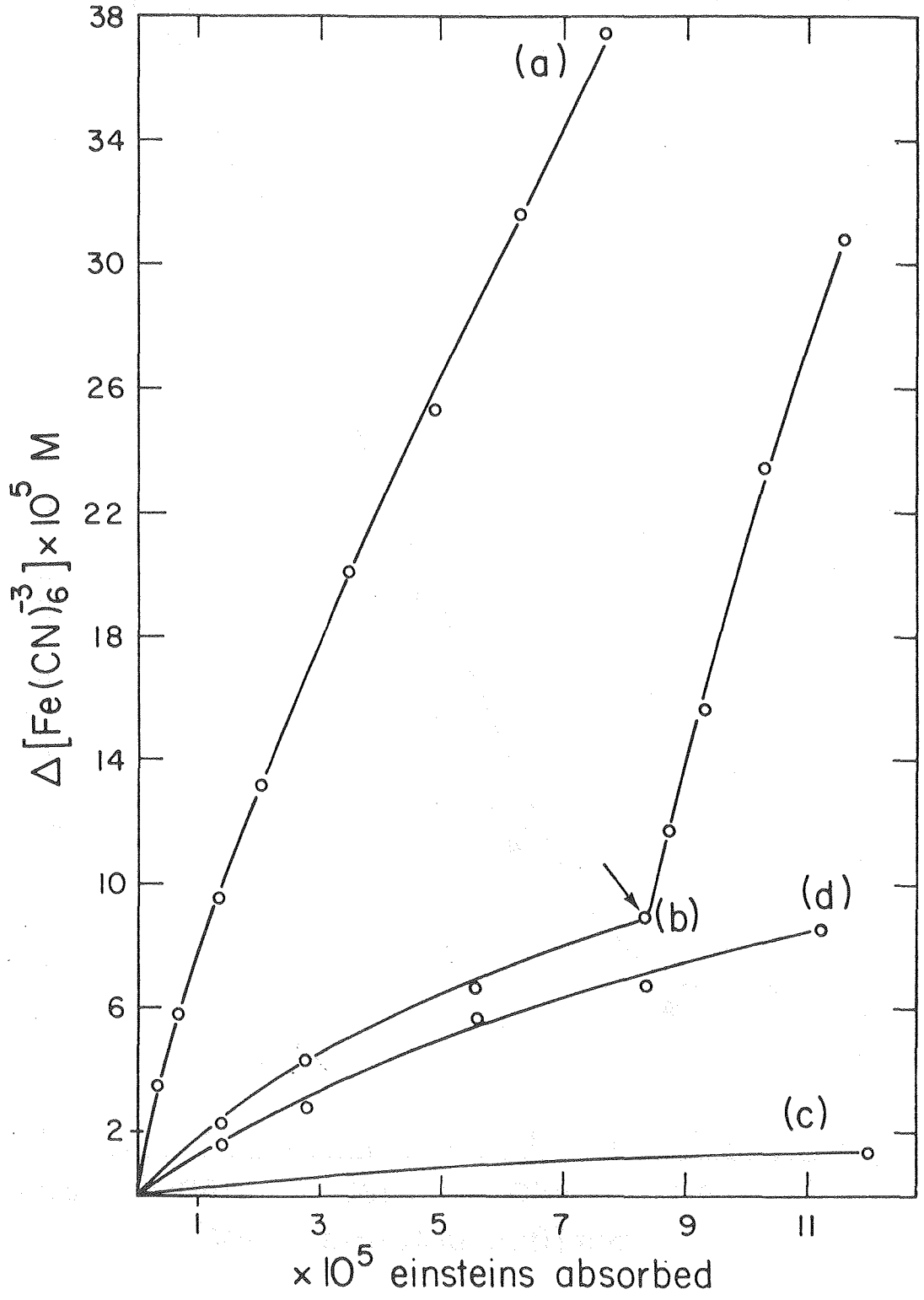


Figure 9. Schematic function of SiO_2 particles in separating multicharged photoproducts

XBL 812-4456



XBL 812-4455

Figure 10. Reduction of $K_3Fe(CN)_6$ as a function of light adsorbed. (a) SiO_2 system including PVS^o; (b) SiO_2 system. Arrow indicates the time of PVS^o addition; (c) homogeneous system; (d) NaLS micellar system

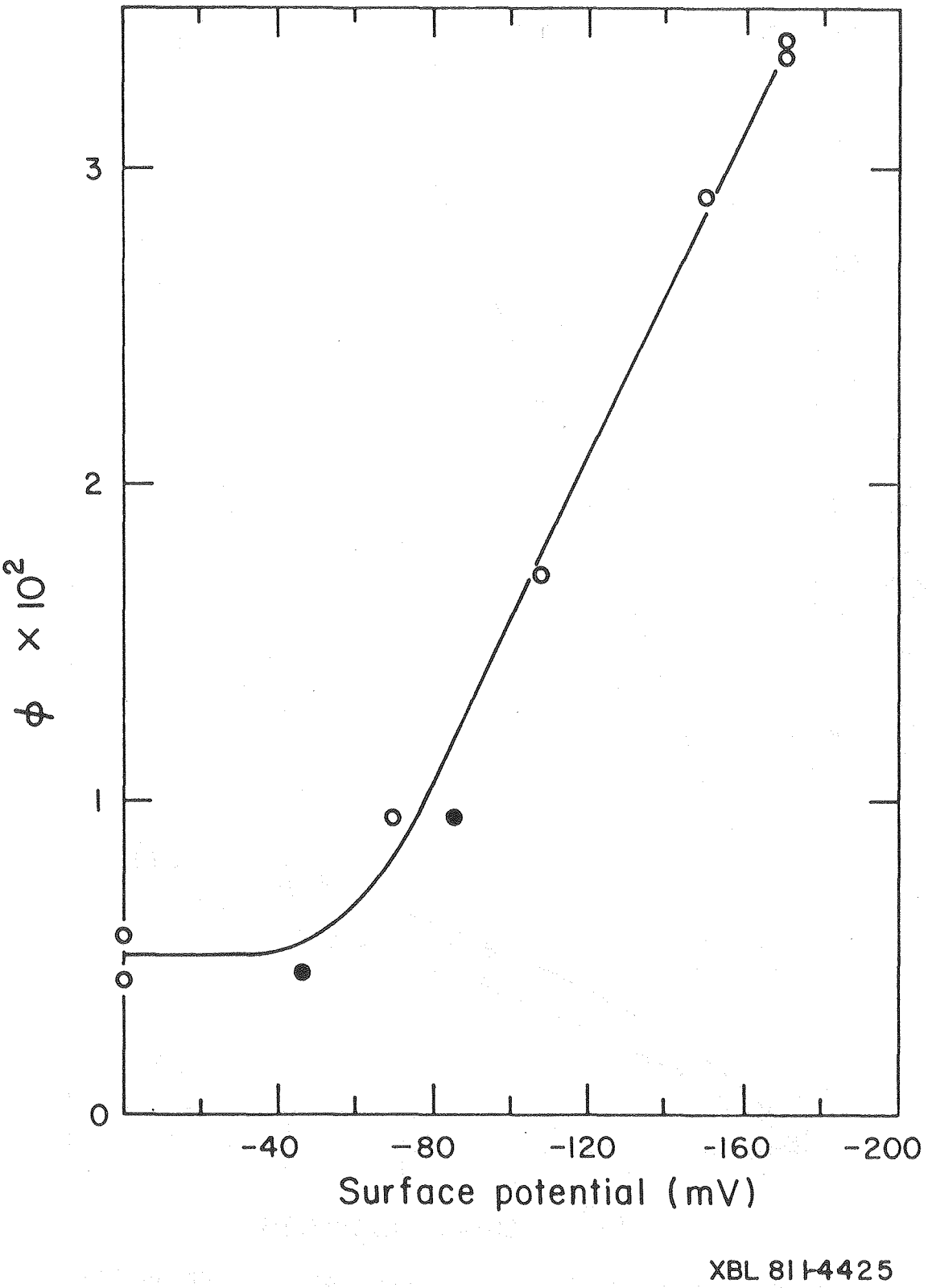
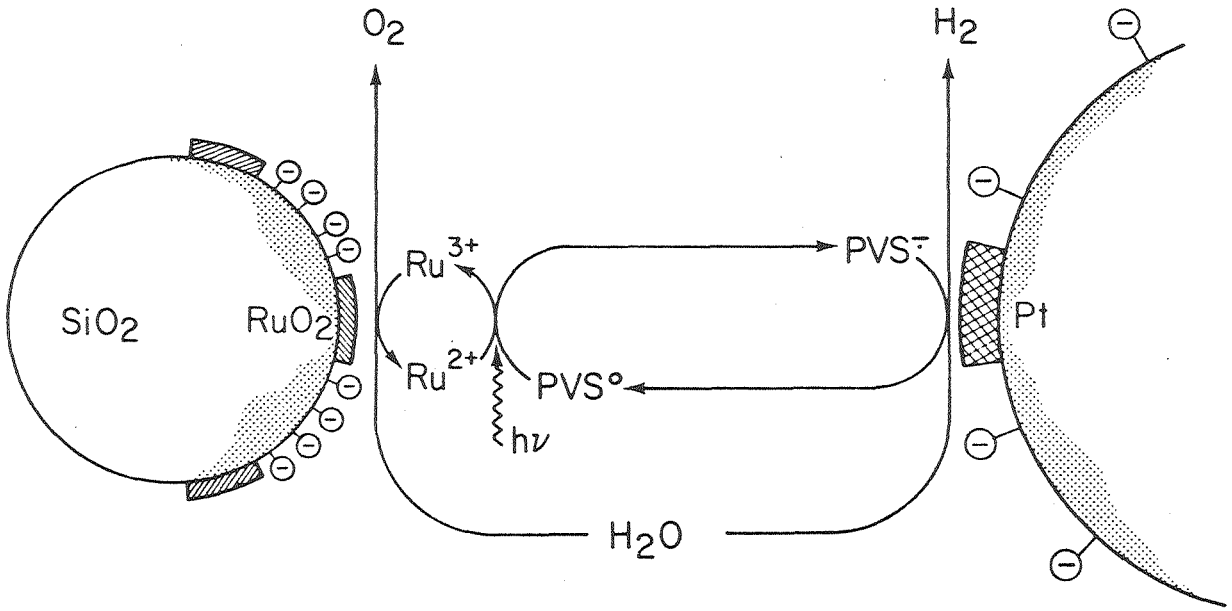


Figure 11. Quantum yield for propylviologen, $PVS^{\cdot}$, formation as a function of the surface potential of negatively charged interfaces (o) SiO_2 system; (●) NaLS micellar system.



XBL 812-4486

Figure 12. Utilization of SiO_2 colloids in the photodecomposition of water.